IV.A.1a DOE Metal Hydride Center of Excellence

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- Georgia Institute of Technology (GT)
- HRL Laboratories, LLC
- Intematix Corp.
- Jet Propulsion Laboratory (JPL)
- National Institute of Standards and Technology (NIST)
- Oak Ridge National Laboratory (ORNL)
- Ohio State University (OSU)
- Sandia National Laboratories (SNL)
- Savannah River National Laboratory (SRNL)
- Stanford University
- United Technologies Research Center (UTRC)
- University of Hawaii at Manoa
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Introduction

The DOE Metal Hydride Center of Excellence (MHCoE) consists of 10 Universities (Caltech, Georgia Tech, Stanford, University of Hawaii, University of Illinois at Urbana-Champaign, University of Nevada, Reno, University of New Brunswick, University of Pittsburgh, Ohio State University and the University of Utah), six National Laboratories (Brookhaven National Laboratory, Jet Propulsion Laboratory, National Institute of Standards and Technology, Oak Ridge National Laboratory, Sandia National Laboratories, and Savannah River National Laboratory) as well as three industrial partners (GE Global Research, HRL Laboratories, and Intematix). SNL is the lead laboratory, providing technical leadership for the center and a center structure to guide the overall technical program and advise the DOE.

In June of 2007, United Technologies Research Center was added as a partner to work on nanoengineering. In June of 2008, Intematix completed its work in the MHCoE, and withdrew from the Center. In addition, GE ended its participation in the Center as of December 2007 and the GE contract was transferred to Ohio State University, with the move of J. C. Zhao from GE to Ohio State. With the move of Prof. David Sholl from Carnegie Mellon University to Georgia Tech, Carnegie Mellon ceases to be a partner, and we added Georgia Tech as a partner. We also added Ohio State University as a partner.

The purpose of the MHCoE is to develop hydrogen storage materials and engineering properties that allow the use of these materials in a way that satisfies the FreedomCAR and Fuel Partnership system requirements for automotive hydrogen storage. In an overall sense, our Center is a multidisciplinary and collaborative effort with the collaborations divided into three broad areas: mechanisms and modeling (which provide a theoretically driven basis for pursuing new materials), materials development (in which new materials are synthesized and characterized) and system design and engineering (which allow these new materials to be realized as practical automotive hydrogen storage systems). Driving all of this work are the hydrogen storage system specifications outlined by the FreedomCAR and Fuel Partnership for 2010 and 2015.

The MHCoE is organized as indicated in Figure 1.

During the past year, the technical work was divided into five project areas. The purpose of the project

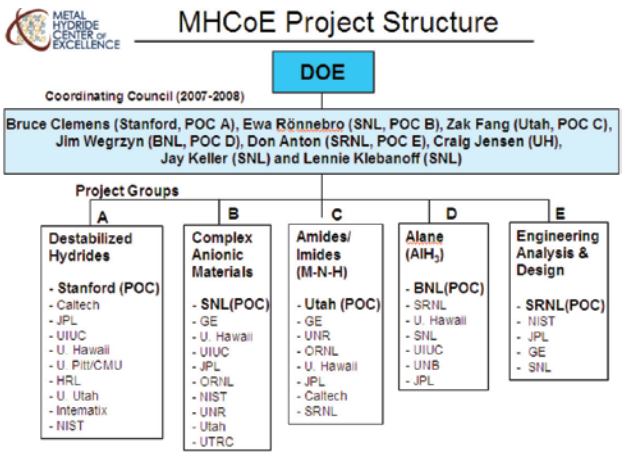

FIGURE 1. Organization of the MHCoE, with Project Areas Given

areas is to organize the MHCoE technical work along appropriate and flexible technical lines.

Project A (Destabilized Hydrides) is led by Prof. Bruce Clemens, Stanford University. The objective of this project is to develop strategies for reducing hydrogen storage thermal requirements and improve kinetics by destabilizing metal hydrides systems. The technical approach is to alter the thermodynamics of the storage system by destabilizing the metal hydride through alloying, thereby reducing the energy needed to liberate hydrogen from the material, and reducing the desorption temperature. The project aims to enhance kinetics by evaluating nanoengineering approaches towards minimizing the required hydrogen diffusion distance by decreasing particle size and creating nano-engineered scaffolds.

Project B (Complex Anionic Materials) is led by Dr. Ewa Rönnebro of SNL. The objective here is to predict and synthesize highly promising new anionic hydride materials. The technical approach involves using theory and chemical intuition to select promising target complex hydrides. Candidate materials are then synthesized by a variety of techniques, followed by extensive structural and hydrogen sorption characterization. A particular focus in Fiscal Year 2008 has been on borohydride materials.

Project C (Amides/Imides Storage Materials) is led by Prof. Zak Fang of the University of Utah. The objective of Project C is to assess the viability of amides and imides (materials containing–NH_2 and–NH moieties, respectively) for onboard hydrogen storage. The technical approach is to reduce thermal requirements of these materials by alloying, understand and elucidate the chemical pathways by which these materials release and absorb hydrogen, and determine the initial engineering issues (thermal cycling) of these materials.

Project D (Alane, AlH_3) is headed by Dr. Jim Wegrzyn of BNL. The objective of Project D is to understand the sorption and regeneration properties of alane (AlH_3) for hydrogen storage. The technical approach has been to synthesize the various structural forms of AlH_3, and characterize the structure and hydrogen sorption properties of these forms. The emphasis in FY 2008 has been on regenerating AlH_3 from Al, using solution-based, electrochemical, and supercritical fluid methods.

Project E (Engineering Analysis and Design) is led by Dr. Don Anton of SRNL. The objective of Project E is to provide engineering analysis and design supporting DOE system performance goals. The technical approach has been to develop engineering system-level storage models, use theory and modeling to provide target materials properties, perform thermal modeling of candidate hydride materials, and conduct expansion, heat transfer and stress measurements of promising materials. One focus in FY 2008 has been on understanding thermal issues associated with hydrogen dispensing stations.

During June of 2008, Project E was discontinued, as much of the MHCoE Project E technical scope will be transferred to the upcoming DOE Hydrogen Storage Engineering Center of Excellence. We will retain in the MHCoE an "Engineering Materials Properties" activity, which will consider engineering-related issues such as material thermal conductivity and cycling behavior in the presence of contaminants.

In addition to these formal "Projects", we have three working subgroups in the MHCoE. The MHCoE Theory Group (TG) is coordinated by Dr. Mark Allendorf (SNL), and makes use of first-principles methods to predict new materials and their thermodynamic properties, and suggests new directions for experimentalists and interpretation of their results. The TG consists of researchers at five institutions: SNL, Pitt/GT, UIUC, NIST and UTRC. To make maximum use of the different areas of expertise, joint TG efforts are guided by SNL not only in terms of technical direction, but also to ensure that TG efforts are complementary and have an effective synergism with experimentalists.

A second working group in the MHCoE is the "Additive Screening Group". This group, coordinated by Dr. Eric Majzoub (University of Missouri at St. Louis, on leave from SNL) examines the effects of catalysts and other additives on the kinetic and thermodynamic properties of metal hydrides. The group makes use of 18 kinetics stations, Sieverts apparatus, and pressure-composition-temperture instruments to screen many catalysts and additives for their effects on hydrogen desorption temperature, kinetics of adsorption/desorption, and material reversibility. This group involves almost all experimentalists in the MHCoE.

The third working group is the Engineering Materials Properties subgroup, mentioned above. This group, coordinated by Dr. Don Anton (SRNL), will foster communication and complementary work by those involved in these applied engineering materials problems. The subgroup includes SRNL, JPL, and NIST.

MHCoE Objectives

Our highest level objective is to:

- Develop new reversible hydrogen storage materials to meet or exceed FreedomCAR and Fuel Partnership 2010 and 2015 system goals.

Technical Barriers

The MHCoE tackles well-defined technical barriers associated with reversible solid-state hydrogen storage systems in which hydrogen is desorbed and re-absorbed

on board the vehicle. These barriers are reproduced below from the Onboard Hydrogen Storage section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

(A) Cost. Low-cost materials and components for hydrogen storage systems are needed, as well as low-cost, high-volume manufacturing methods.

(B) Weight and Volume. Materials and components are needed that allow compact, lightweight, hydrogen storage systems while enabling greater than 300-mile range in all light-duty vehicle platforms. Reducing weight and volume of thermal management components is required.

(C) Efficiency. The energy required to get hydrogen in and out of the material is an issue for reversible solid-state materials. Thermal management for charging and releasing hydrogen from the storage system needs to be optimized to increase overall efficiency.

(D) Durability. Materials and components are needed that allow hydrogen storage systems a lifetime of 1,500 cycles with tolerance to fuel contaminants.

(E) Refueling Time. There is a need to develop hydrogen storage systems for the refueling times of less than three minutes for 5 kg of hydrogen, over the lifetime of the system. Thermal management during refueling is a critical issue that must be addressed.

(G) System Life Cycle Assessments. Assessments of the full life-cycle, costs, efficiency, and environmental impact for hydrogen storage systems are lacking.

Technical Targets Addressed by MHCoE

While all of the targets detailed in the DOE Multi-Year Research, Development and Demonstration Plan will be addressed, our main emphasis initially focuses on the DOE specifications for system specific energy density (2.0 kWh/kg [2010], 3.0 kWh/kg [2015]) and system volumetric energy density (1.5 kWh/L [2010], 2.7 kWh/L [2015]). These targets, in an overall way, drive our "down-select" process for materials. The procedure used to select materials for further study has been documented in following report submitted to DOE:

"Materials Go/No-Go Decisions Made Within the DOE Metal Hydride Center of Excellence (MHCoE), L.E. Klebanoff, October 5, 2007, Summary report posted on DOE Hydrogen Storage Web site: http://www1.eere.energy.gov/hydrogenandfuelcells/hydrogen_publications.html#h2_storage

Selected MHCoE Technical Highlights for FY 2008

During the past year, the MHCoE has published 60 papers (25 of these collaborations between MHCoE partners) in the leading journals of chemistry, physics, materials science and crystallography. In addition, MHCoE scientists delivered 97 talks at national and international meetings, and filed four patent applications. MHCoE scientists are professional leaders in the general field of hydrogen interactions with materials.

Below we present selected highlights from the MHCoE technical work over the period March 2007-March 2008. Please consult the partner's individual annual reports (following) for more details.

- Measured a 60-fold increase in hydrogen desorption rate when $LiBH_4$ was incorporated into carbon aerogel (HRL, Project A).
- Developed a low-temperature, organometallic method for high level 16% loading of Al and Mg in carbon aerogels without host degradation (University of Hawaii, Project A).
- Using in situ X-ray diffraction we made the first quantitative determination of structural changes and associated changes in uptake and release kinetics associated with cycling by utilizing thin epitaxial Mg films as a model system (Stanford, Project A).
- Validated combinatorial catalyst deposition (sputtering) and optical screening techniques on slurry deposited metal hydrides by observing transitions at 190°C for $NaAlH_4$, and 160°C for Ti on $NaAlH_4$ (Int*e*matix, Project A).
- Developed new theoretical method for accurate density functional theory prediction of reaction enthalpies in molecular solids, eliminating previous limitations and errors (UIUC, Project A).
- Quasielastic neutron scattering studies of $LiBH_4$ nanoconfined in carbon aerogels indicated a higher BH_4^- rotational mobility than in the bulk, with significantly reduced rotational activation energy (NIST, Project A).
- Investigated the ScH_2-$2LiBH_4$ system predicted by MHCoE theorists to have an enthalpy of dehydrogenation of 34 kJ/mole system. The predicted dehydrogenation reaction products are not discernable via X-ray or nuclear magnetic resonance. We attribute this to high formation enthalpies of ScH_2 and ScB_2. (Caltech, Project A).
- Implemented a theoretical method to identify the lowest energy reaction pathways for families of complex hydrides, and used this method to scan reactions covering over 16 million compositions as a function of temperature (Pitt/GT, Project B).

- Determined the crystal structures and phase transitions of $Ca(BH_4)_2$ polymorphs at different temperatures (SNL, Project B).
- Used prototype electrostatic ground state (PEGS) theory to predict two bialkali borohydrides, $NaK(BH_4)_2$, and $LiK(BH_4)_2$ (which were synthesized by mechanical alloying). PEGS also provided the best candidate for the ground state crystal structure of $Mg(BH_4)_2$ (SNL, Project B).
- Elucidated the desorption process of $Mg(BH_4)_2$. Using five independent techniques, discovered the formation of an amorphous $MgB_{12}H_{12}$ intermediate phase, and discovered reversible behavior at about 300˚C and 100 bar H_2 pressure from $Mg(BH_4)_2$ to $Mg(BH_4)_{2-x}$ during the initial decomposition process of $Mg(BH_4)_2$ (GE, Project B).
- Completed study of temperature dependence of H_2/B_2H_6 ratio during decomposition of $Al(BH_4)_3$ (ORNL, Project B).
- Conducted compatibility screening on a combination of $LiBH_4$ and nine different candidate framework materials including SiO_2, Al_2O_3 and ZrO_2 (UTRC, Project B).
- Conducted in-depth study of the hydrogen storage behavior of LiMgN and the influence of process variables on the hydrogen storage reactions involving $LiNH_2$ and Li_3AlH_6 (University of Utah, Project C).
- The reversibility of LiMgN has been confirmed with maximum absorption of 3.5 wt% occurring a 180°C at 140 bar pressure after six hrs. Rehydrogenation products were identified as $LiH+Mg(NH_2)_2$ (SRNL, Project C).
- Studied the effects of impurities on the cycling stability of Li_2NH-$LiNH_2$. The material was exposed to 100 ppm levels of contaminants such as O_2, CO, H_2O, and CH_4, in H_2 and industrial hydrogen, up to ~1,100 cycles. Oxygen was most detrimental to the cycling behavior of amide-imide hydrides. The H_2O (100 ppm) impurity surprisingly produced lower degradation as compared with oxygen (100 ppm) impurity (UNR, Project C).
- Demonstrated a liquid-phase approach for producing aluminum hydride from aluminum and hydrogen. The two step process involves first making lithium alanate from aluminum, hydrogen and lithium hydride in a liquid solvent. The second step is recovering aluminum hydride from lithium alanate and recycling the lithium hydride byproduct (BNL, Project D).
- Used quantum chemistry calculations to identify several alane-amine complexes that should promote AlH_3 harvesting efforts by BNL (SNL, Project D).
- Developed an improved supercritical fluid medium for the hydrogenation of Al such that 5% of the Al is converted to AlH_3 (University of Hawaii/UNB, Project D).
- Synthesized multiple gram quantities of very pure AlH_3-triethylenediamine using electrochemical charging of solvated $NaAlH_4$ (SRNL, Project D).

Awards and Honors

The theoretical work of the University of Pittsburgh (Johnson), and Georgia Tech (Sholl, Dai) was awarded the 2008 DOE Hydrogen Program R&D Award, "In recognition of outstanding contributions to hydrogen storage technologies."

Acknowledgement

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